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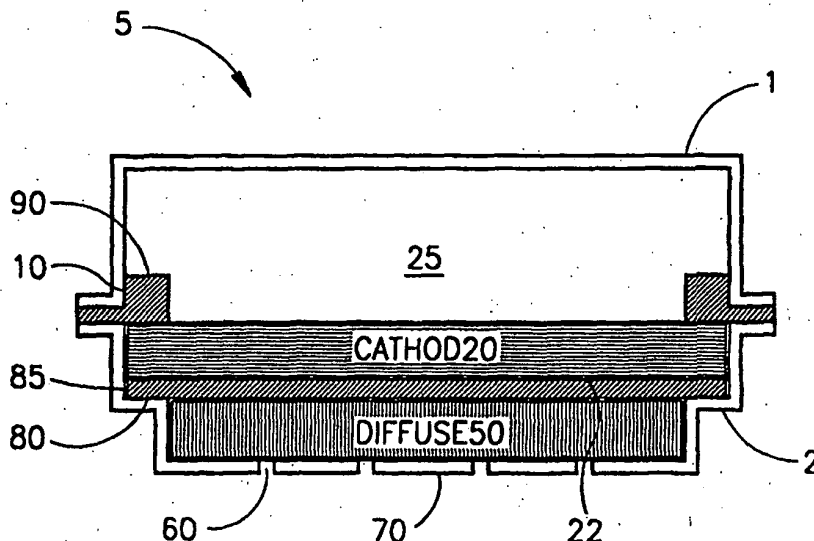
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(54) Title: CORROSION RESISTANT HIGH PERFORMANCE ELECTROCHEMICAL CELL



(57) Abstract

Particle-size-selected metal is mixed with an electrolyte and used as a combined anode/electrolyte in a metal-alkaline battery cell. The particles in the particle-size-selected metal are selected so that substantially all of the particles are larger than a predetermined size. The resulting battery cell exhibits improved corrosion and shock-resisting properties, as compared to when metal particles that have not been size-selected are used. In a preferred embodiment, zinc is used as the particle-size-selected metal to form a zinc-air battery.

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5 **CORROSION RESISTANT HIGH PERFORMANCE
ELECTROCHEMICAL CELL**

CROSS REFERENCE TO RELATED APPLICATIONS

Priority is claimed to U.S. application No. U.S. application No. 60/112,292, filed on December 15, 1998; and U.S. application No. 60/129,401, filed on April 15, 1999, and each of these applications is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

The present invention relates to zinc-based alloys and electrolyte additives providing resistance to corrosion and improved performance as an electrode in electrochemical cells.

15 The invention also relates to materials for housing electrochemical cells that ameliorate corrosion problems. The present invention is particularly applicable for zinc-based alloys for use in metal-air battery cells.

In conventional zinc-air batteries, the cathode reduces ambient oxygen, which means that the battery has only a single consumable electrode. The cathode of a metal-air battery typically has an active layer of activated carbon, a catalyst, and a binder, which forms a network and holds the carbon together. Embedded within the active layer is a metal current collector. A guard layer covers the surface of the active layer that faces the outside air, and an ionically conducting separator covers the surface that faces the anode. The guard layer keeps electrolyte from leaking out of the cell, and the separator separates the anode or an electrically conductive reaction product from the cathode active layer, thereby preventing an electrical short.

Polytetrafluoroethylene (PTFE) is an example of a suitable material for a binder, and manganese oxides and hydroxides are commonly used catalysts. A nickel screen is a commonly used current collector although an expanded metal sheet or an alternative conductive material can be used, instead. The guard layer can be made of a sheet of porous PTFE, and the separator can be made of a semipermeable membrane or a porous material.

Zinc-alkaline cells are known in the art as safe power sources having very high energy densities. One class of such cells - namely, zinc-air cells - can use ambient oxygen as one of their electrodes, which eliminates the need for such cells to house two consumable electrodes in the same casing. Along with the benefits of metal-alkaline cells comes the drawback of the anode's tendency to corrode, particularly in the presence of dissimilar metals and electrolytes. Also, metal-alkaline batteries suffer from relatively poor performance in low temperature environments.

One example of metal alkaline cells, namely zinc air cells, are capable of very high energy densities. The components of zinc-air cells are typically lightweight and inexpensive. Although zinc-air cells have high energy density, their power capacity is not extremely high and this is unfortunate since many electronic portable devices demand relatively large amounts of power from their power sources.

A known technique for enhancing power performance in metal-alkaline cells is to provide high reaction rates by subdividing the metal as finely as possible or using crystalline forms characterized by high surface to mass ratio. Electrolytic zinc derives its ability to increase its power through its very high surface area to mass ratio. Unfortunately, the higher surface area also contributes to increased corrosion rates. It is known to alloy metals such as zinc with metals that reduce the corrosion rate. However, electrolytic zinc cannot be alloyed easily because of the way it is formed.

Thermal zinc (powdered zinc formed by atomization) is susceptible to alloying. However, thermal zinc cannot, at present, approach electrolytic zinc's surface area to mass ratio.

Zinc-air battery cells typically have casings made, at least partly, of metal. The beneficial material properties of metal include its ability to serve the multiple purposes of housing the electrode(s), serving as electrical terminal(s) of the cell, and as providing a large surface area to act as a low resistance current collector. Its value as a housing material derives from its cost, manufacturability, strength, and other features. Cells can be made from two electrically insulated metal casing elements, which act as the opposing terminals of the cell, making the cell easy to electrically connect with an electronic device. Further, metal casings are inexpensive to manufacture, sometimes requiring only a simple stamping operation of a thin sheet of metal to form a relatively precisely shaped casing element.

Metal casings can exacerbate corrosion by forming a galvanic process with the zinc and the electrolyte. Corrosion wastes the cell's energy by consuming the zinc anode. Certain

agents have been found to reduce the corrosive effects. However, these corrosion-inhibiting agents create certain difficulties and tend to inhibit the power capacity of the cell.

The parasitic corrosion of zinc produces hydrogen gas. Hydrogen, if not permitted to escape from the casing of the cell, can cause the internal pressure of the cell to rise. An increase in the internal pressure of the cell can cause the cell to electrically short, swell, leak electrolyte, and potentially burst.

Zinc-air battery cells typically perform poorly in low temperature environments. As the temperature decreases, the viscosity of the electrolyte increases, which can lower the power capacity and overall energy capacity (given a minimum-voltage requirement for usability) of the cells.

Zinc-air battery cells are also susceptible to failure due to sudden shocks. Sudden shocks can significantly and temporarily reduce the discharge voltage of the cell. These shocks can cause the electronic device to temporarily lose power. In certain applications, a temporary loss of power can have significant adverse effects. For example, a transient loss of power in a cellular phone may result in disconnection.

SUMMARY OF THE INVENTION

It is a principal object of the invention to provide an electrochemical cell having zinc electrodes with improved corrosion resistance and higher performance, particularly at low temperatures. It is a further object of the invention to provide a metal casing that can eliminate or significantly inhibit the reactivity between a zinc-based anode and a metal casing.

Electrolytic zinc, with its high current generation potential, is mixed with thermal zinc, which can then be mixed with corrosion-inhibiting agents. In the alternative, the corrosion-inhibiting agents can also be alloyed with the thermal zinc, during its formation or otherwise, and then be combined with electrolytic zinc. In the formation of pure electrolytic zinc, the corrosion-inhibiting metals are less prone to alloy with the zinc anode. The addition of these agents significantly reduces the rate at which the zinc corrodes.

In certain mixtures of electrolytic/thermal zinc, the two types of zinc can be mixed together and pressed to form into a plaque. The formation of a plaque may eliminate the need to add a gelling agent. The result is a somewhat rigid structure that is capable of being placed in the cell instead of being extruded in the cell. The structure of the zinc significantly improves the manufacturability of the cell.

A typical tri-clad metal casing is made of layers of nickel, stainless steel, and copper, with the layer of copper on the inner surface of the casing element and the layer of nickel on the outer surface of the casing element. The combination provides strength via the stainless steel, better electrical connectivity through the addition of the nickel, and a reduction in the chemical reactivity between the layer of stainless steel and the zinc anode through the use of copper. A layer of tin on top of the layer of copper can further reduce the rate of corrosive activity by separating the zinc/electrolyte mixture from the metal casing. This layer can be added by soldering, electrolytic plating, or by an electroless process.

The performance of the zinc anode, especially in low temperature environments, can improve through the addition of low viscosity diluents and/or alumina. The addition of diluents such as isopropanol have been found to increase the discharge voltage of the cell with a minor decrease in energy capacity. The addition of alumina increases the energy capacity of the cell by up to 20%. The combination provides both benefits.

The invention will be described in connection with certain preferred embodiments, with reference to the following illustrative figures so that it may be more fully understood.

With reference to the figures, it is stressed that the particulars shown are by way of example and for purposes of illustrative discussion of the preferred embodiments of the present invention only, and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention. In this regard, no attempt is made to show structural details of the invention in more detail than is necessary for a fundamental understanding of the invention, the description taken with the drawings making apparent to those skilled in the art how the several forms of the invention may be embodied in practice.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is graphical representation of discharge voltages of two similarly sized battery cells with zinc anodes having a different porosity.

Fig. 2 is graphical representation of the discharge voltages of five similarly sized battery cells with zinc anodes having different porosity and polyethylene glycol (PEG) content. The representation shows the effect that a sudden jolt has on differently configured battery cells.

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Figs. 3 and 4 show the effect that the additions of a diluent and alumina to a metal

anode have on the performance of a battery cell exposed to a low temperature environment.

Fig. 5 shows a cross-sectional representation of a tri-clad metal anode casing element of successive layers of nickel, stainless steel, and copper.

Fig. 6 shows an alternative cross-sectional representation of a tri-clad metal anode casing element with a layer of copper on both sides of a layer of stainless steel.

Fig. 7 is a schematic section view of a typical zinc-air battery cell that can make use of the air cathode of the present invention. The schematic is intended only to illustrate relationships between various components.

Fig. 8 is schematic section, partial perspective, view of an air cathode illustrating some of the embodiments of the invention.

DESCRIPTION OF THE INVENTION

The cathode described herein is intended for use in electrochemical cells or fuel cells. It is especially intended for use in primary metal-air battery cells, and especially zinc-air cells. The cells may be any suitable shape and be arranged in a housing that is liberally supplied with openings to allow air gases to be exchanged between the ambient air and the enclosed cells. The cells can have a housing of metal, plastic, or any other suitable material. Each cell may have an array of air holes, such as used in zinc-air button cells, in such number and size as to allow oxygen to be supplied to a cathode inside the cell. The air holes of each cell may face either a plenum or the casing wall. The air holes are uniformly distributed, sized, and present in such number so as to insure that the cathode is not starved for oxygen, which could cause a drop in voltage. As an alternative to holes, the cell may use a semipermeable membrane or structure that permits the diffusion of gases through the membrane or structure.

Referring to Fig. 7, each of the cells 5 contains at least one air cathode 20 and at least one zinc anode 25 with aqueous alkaline electrolyte (e.g., KOH). The cathode 20 lies adjacent a cathode side of the cell casing 2 and may be separated from that side by a diffuser 50. The diffuser 50 distributes oxygen from holes 60 in the cathode side of the cell 2 across the surface of the cathode 20 and keeps the cathode 20 at a fixed distance, equal to the diffuser's 50 thickness, from the cathode side 2 of the cell 5. The diffuser 50 may be a porous material such as woven, knitted, or non-woven cloth or extended plastic mesh material. It may act as a standoff to prevent the air-side surface 22 of the cathode 20 from smothering any of the holes 60 when an expansion of the zinc anode 25 causes the surface to press against the

inside wall of the cathode side of the cell 2. The holes 60 in the cathode side of the cell 2 are uniformly distributed across the primary plane 70 of the cathode side of the cell.

The casing 1 / 2 of the cell may be formed in two halves, an anode side 1 and a cathode side 2 as in Fig. 7. The cell casing 1 / 2, may be formed of any suitable material. If the casing 1 / 2 is made of metal or any other conductive material, the two halves 1 and 2 should be insulated from one another. In either case, to form a primary seal 80, the cathode 20 may be attached to, or sealed against, the cathode side 2 of the cell casing 1 / 2. The primary seal 80 may be effected by pressure, adhesive, or any other suitable means to prevent liquid electrolyte from leaking into the space occupied by the diffuser 50. That is, the primary seal 80 prevents liquid electrolyte from seeping around the cathode 20 into the area exposed to the outside air. A secondary seal 10 between the anode side of the cell 1 and the cathode side 2 prevents aqueous electrolyte from seeping around to the edge of the cathode 20 or leaking out of the cell 5. In the embodiment of Fig. 7, the secondary seal 10 is formed by a grommet 90, which also serves to insulate the anode side 1 and cathode side 2 of the cell casing 1 / 2 from each other. Pressure, an adhesive, or flowing sealant, or other suitable means may be used to effect the secondary seal 10.

Referring to Fig. 8, in an embodiment, the cathode consists of multiple layers with the middle layer being an active layer 120 composed primarily of carbon, PTFE, and a catalyst for reducing oxygen. Note that Fig. 8 is not to scale. The active layer 120 is the location where the oxygen reduction reaction takes place in the presence of the catalyst. A separator layer 100 which may be prelaminated to the active layer 120 can be made from microporous hydrophilic polypropylene (PP), polyethylene, PVC, cellophane, nylon, Celgard®, or other materials exhibiting similar properties. In some applications, the pore size of the separator 100 is in the range of about 0.25 micron to 2 microns instead of the more typical average pore size of less than 0.25 micron used in other battery applications. The larger pore size is sufficient to limit electrical shorts from crystallization of zinc oxide in the separator layer 100, and still permit enhanced wetting of the cathode active layer 120 with KOH solution. Other types of separator materials that may provide better cathode performance include microporous polyethylene or polypropylene whose hydrophilicities are enhanced by radiation grafting. Another class of suitable separator materials is semipermeable membranes based on cellophane, polyethylene, PVC, nylon, and polypropylene, for example, ZAMM-0 supplied by Pall RAI Corp. An additional non-woven, absorbent material can be added between the air

electrode and the microporous separator or between the microporous separator and the zinc. The purpose of this is to provide an electrolyte reservoir.

The following processes may provide the preferred composition of the electrode active layer 120. The quantities are representative only and the quantities and proportions may be varied.

1. 240 g MnO_2 powder (Aldrich Chemical Company, Milwaukee, WI) is milled for 24 hours.
2. Add 2000 cc deionized water and heat to 85°C while stirring.
3. Slowly add 800 g activated carbon (Darco G-60 from American Norit, Atlanta GA).
4. Slowly add 288 cc PTFE suspension (grade 30-N from DuPont).
5. Continue stirring for an hour.
6. Filter and then dry at 120°C for about 5 hours.

An alternative process for making an active layer that starts with KMnO_4 instead of MnO_2 is described in US Patent 3,948,684, the entirety of which is incorporated herein by reference.

Embedded within the active layer 120 is a current collector 140 commonly formed of a metal, for example, a nickel, screen. Nickel-plated or nickel-clad steel, gold-plated metal, or other materials could also be used. A plastic element coated or clad with a conductor could even be used. It is preferred that the current collector 140 of the cathode be treated or constructed in such a way as to provide high surface area and low electrical resistance. The formation of oxide on the surface of a metal mesh current collector or a thin film of electrolyte on the hydrophilic surface of the current collector may limit the power capacity of the battery cell. One way to deal with this is to coat the current collector with a coating of a non-corroding metal finish. However, merely coating the current collector will not eliminate the disadvantages of remaining hydrophilic. Another option is to paint the electrode with a hydrophobic conductive paint. Hydrophobic conductive paints have other advantages over metal finishes. Gold and silver are the only metals that can be coated on a cathode mesh and still provide reasonable conductivity. Both are very expensive. Moreover, a silver coating is slightly soluble in alkaline electrolytes, which may lead to an increased corrosion of the zinc anode.

This paint may be applied before the cathode active layer is combined with the current collector. A preferred paint is a mixture of the following:

1. Fluorinated ethylene propylene copolymer (FEP) (Dupont 120-N or 121A) or some other thermoplastic, (e.g. polyolefin) preferably a fluoropolymer.
2. Isopropyl alcohol or some other suitable solvent (other alcohols, ketones, chlorinated hydrocarbons, etc.)
3. Acetylene carbon (Shawinigan carbon black made by Chevron) or some other suitable form of carbon, preferably hydrophobic, such as graphite.

A representative batch of paint may be formed of 1400 cc isopropyl alcohol, 108 cc FEP and 20 g acetylene black. The paint may be sprayed, or applied by any alternative suitable means, onto a mesh at a loading of 0.72 mg/cm^2 . This loading is only an example, and higher or lower loading values may also be used. The coated mesh is then baked in an oven at $290\text{--}330^\circ\text{C}$ to sinter the FEP and bond it to the metal current collector, e.g., woven nickel mesh. The actual sintering temperature, in applications of the present invention, may depend upon the particular thermoplastic used. Note that, in addition to sintering a sinterable material such as FEP, materials that can be melted to form a coherent mass could also be used in replacement of the sinterable material to bond the coating in place. The painted current collector may be heated by microwave, infrared, RF, or ultrasonic means instead of heating the coated mesh in an oven. The sintered coating forms a continuous hydrophobic conducting coating that protects against the corrosion or the oxidation of the metal mesh material. The sintering step also removes the surfactant in the FEP emulsion. It has been found that an air electrode with this coating laminated to a suitable separator and then incorporated into a zinc-air cell of area 10 cm^2 (2.5 cm. by 4 cm.) gave a steady state voltage 250 mV higher than an air electrode without this coating when discharged at a constant 0.47A.

To provide for high current capability in zinc-air batteries, the cathode should be fully saturated with electrolyte. The cathode tends to dry out as a result of water evaporating from the cell and as a result of waters of hydration being drawn away from the cathode when zinc oxide forms during discharge of the cell. The addition of hydrophilic agents to the cathode ameliorates this dryout effect. For example, cellulosic materials such as Natrosol @ 250 MBR hydroxyethylcellulose (HEC) may be added to the cathode material (finely divided and added to the active layer mixture). As moisture leaves the cathode during discharge, the HEC holds onto this moisture and makes it available in the cathode despite the progressive drying of the cathode. A similar material has been used as a monolithic layer, but the incorporation

of the material in its finely divided form inside the cathode active layer helps to insure that moisture is held where it is needed. The following is an example construction of a cathode material using Natrosol.

5 240 g. of MnO_2 powder (Aldrich Chemical Company, Milwaukee, WI) is ground finely in a mill for 24 hours. The MnO_2 is then poured into 2 liters of deionized (DI) water and heated to 85°C . Add 800 g. of Darco G-60 carbon (American Norit, Atlanta GA) while stirring. Then add 288cc of Dupont 30-N PTFE suspension. Continue stirring for one hour, and then filter and dry at 120°C for 5
10 hours.

 Slowly add 200g of the active mass made above to 5 liters of DI water stirred at 85°C . After all the carbon is in suspension, add 2 grams of Natrosol (grade 250MBR from Hercules). Continue stirring under heat until dry.

 The active mass treated with the Natrosol® is spread evenly over a
15 nickel mesh (40x40 mesh 0.005 mm dia. nickel from National Standard) and pressed to make an active layer of an air electrode. A porous PTFE sheet is then pressed on one side of the active layer.

 The air electrode from above is then laminated with a microporous polypropylene film (grade 3501 from Celgard®) separator. The air electrode and
20 separator laminate is then assembled into a zinc-air cell of area 10cm^2 containing 3.1g zinc and 2.4g 8M KOH solution, and the complete cell closed by crimping.

 Testing Technique - The test cell and a control cell that does not contain the Natrosol® are exposed to a 25-30% relative humidity (RH) environment for a period of 7 days. After 7 days the cells are discharged under a load following a
25 GSM profile, which is one of the standard profiles used by mobile communication devices for communicating with ground stations. GSM is a galvanostatic square wave profile consisting of 1.3A for 0.6 msec and 0.08A for 4.0 msec. The discharge cycle spans one hour (0.2Ah). The cells are then returned to the low humidity environment. This discharge cycle is repeated every 3-4 days until the cells fail. Failure is defined
30 as the high current voltage falling below 0.9V.

 Results - On the initial test after 7 days, both types of cells had a voltage above 0.9V. But when tested after a total of 11 days exposure to 25%RH, the

cell without Natrosol® failed. The cell with Natrosol® continued to work in similar tests over a period totaling 25 days in a 25%RH environment.

In Fig. 8, which shows a cross-section of the cathode, there is a guard layer 160, preferably formed of a PTFE film, laminated to the side of the active layer facing the air holes. The guard layer 160 allows oxygen to enter the cathode while preventing liquid electrolyte from leaking out. This layer 160 is preferably unsintered and highly porous to gases. The preferred porosity is at least 30%, but it is desirable to provide a guard layer that is even more porous. Porosity of 50% or more are even more preferable. The preferred thickness of the guard layer is no more than 100 microns.

As visible in Fig. 7, an uncompressed PTFE film 85, which is separate from the laminated structure of the cathode 20, is uncompressed by any laminating process used to form the cathode structure shown in Fig. 8. During the manufacture of the cell, the grommet 90 forces the cathode 20 against the cathode side of the cell 2, thereby compressing the previously uncompressed PTFE film 85. This helps to form the primary seal 80, which isolates the volume of the cell that is in communication with the outside air from the electrolyte as described above. Since the film 85 is initially uncompressed, it can act as a gasket to create or augment the secondary seal. Also, as discussed above, other means may be used to effect the seal 80 and the uncompressed PTFE layer 85 is not essential for this purpose. The PTFE layers – the guard layer laminated to the cathode and the uncompressed layer – allow air to diffuse into the cathode while preventing liquid from leaking out.

In production, the active layer 120, the separator sheet 100, and the guard layer 160 may be laminated together to form a single structure. Representatively, the dimensions of the active layer and the separator layers are 0.20-0.50 mm and 0.025-0.25 mm, respectively. The actual dimensions depend on the application and can be any suitable thickness. It is preferable that the final pressure used to laminate all the layers together not be too high.

It has been found that an active layer density of less than 1 g/cc is a suitable for attaining high current densities. It has been found that an active layer density of 0.8 g/cc is achievable and provides even greater current density potential. It was found that a PTFE layer with a porosity greater than 50% and a thickness less than 100 microns and an active layer with a density less than 1 g/cc, and preferably less than 0.8 g/cc, exhibits a substantially higher limiting current than prior art cathodes. Together, these improvements produce an air electrode with a limiting current greater than 400mA/cm² with a voltage greater than -300mV as compared to a Hg/HgO reference electrode at room temperature.

Still another feature that has been found to result in higher performance is a roughened surface on the cathode active layer facing the separator. Such a surface can be obtained by pressing the surface with an irregularly surfaced mold to form an imprint. Alternatively, various abrasion techniques, such as brushing, air blasting, or sandblasting; or various heat treatments, such as partial oxidation, can be used. The average roughness (R_a) of the surface, as measured by ANSI B46.1-1978, should be on the order of 10-100 microns instead of the usual 0.1-1 microns.

The combining of thermal zinc and electrolytic zinc to form a zinc mixture results in a zinc anode that is capable of generating relatively high current and combining with many performance increasing additives, such as corrosion inhibiting agents. Electrolytic zinc is formed by subjecting zinc to an electrolytic process, which results in a form of zinc that is porous and that has a high surface to mass ratio. The process includes directly electroplating metallic zinc onto a current collector from a solution of zinc ions. The porous zinc that results from the process exhibits superior electrical conductivity and is capable of generating more power than a less porous zinc. Referring to Fig. 1, the graph plots the voltage output over time of two battery cells subjected to the same load. Line A represents the voltage output of a battery cell containing electrolytic zinc, and line B represents a battery cell containing thermal zinc. Fig. 1 clearly shows that electrolytic zinc (Line A) provides an increase of approximately 0.2 volts or approximately 20% to the voltage output of the battery cell.

Although the electrolytic process is beneficial in that it results in a zinc capable of generating high current, the electrolytic process is not suitable for forming particles containing corrosion inhibiting metals alloyed to the zinc. Thermal zinc, on the other hand, is capable of combining with corrosion inhibiting agents and is formed by atomizing molten zinc to form a zinc powder having a particle size distribution of between 0.0075 to 0.8 mm and a surface area of between 0.2 - 0.4 m²/g. Thermal zinc can then be combined with corrosion inhibitors, a gelling agent and a KOH solution to form a gelled mass capable of being extruded to form a zinc anode.

A mixture of thermal zinc with electrolytic zinc results in a combination exhibiting beneficial qualities of both thermal and electrolytic zinc. A gelling agent may be added to the mixture to form a zinc slurry. A mixture containing 10% to 50% electrolytic zinc is preferable.

At the higher end of the spectrum (50% electrolytic zinc), a gelling agent may not be necessary. The mixture can be combined and pressed together to form a porous, rigid, plaque.

The plaque maintains its shape due to the dendritic structure of electrolytic zinc tangling with the structure of the thermal zinc. The dendritic branches of electrolytic zinc tangle with each other and also with the thermal zinc to hold the powder-like thermal zinc. One advantage of forming a plaque structure is that the plaque can be placed in the casing. Normally, a gel-like, zinc bolus is dispensed in the casing and the manufacturer must provide time in the assembly process for the zinc to settle and spread out to fill the casing.

The addition of polyethylene glycol (PEG) to the zinc electrolyte mixture can reduce the rate by which the zinc corrodes. The effect of PEG on zinc corrosion was evaluated using PEGs with differing molecular weights. Referring to Table 1 below, PEG-600 and PEG-1500 were found to be most effective in this demonstration, with higher concentrations resulting in better corrosion resistance.

TABLE 1

Concentration, ppm	Corrosion rate (%/week)		
	PEG-600	PEG-1500	PEG-10,000
500	0.009	0.007	0.017
1000	0.008		0.018
1500	0.006	0.006	0.017
2500	0.005	0.006	0.018
3000	0.006	0.006	0.018
4000	0.004	0.004	0.017
5000	0.002	0.004	0.016

The addition of PEG to the zinc anode also increases the cell's resistance to sudden shocks. Sudden mechanical shocks to the cell can cause the discharge voltage to significantly and temporarily drop. This voltage drop can significantly and adversely affect the operation of the device powered by the cell. The effect is more pronounced in zinc-air cells with zinc anodes made of electrolytic zinc.

A large minimum particle size can contribute substantially to a low corrosion rate. A particular zinc anode material was obtained by removing the smallest fraction of particles, those below 100 microns, from a batch of zinc particles. In test samples, the starting material

was Mitsui thermal zinc, 50 to 500 microns. The smallest fraction, below 75 microns, was removed by sieving. The results of tests of samples of the big zinc particles shows a very low corrosion rate. The following are results of corrosion tests on various batches of zinc material, some in combination with PEG or PbO.

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Table 2

No	Type	IR	Rp	V _{plat}	Cap [Ah]	Corrosion rate (%/wk)		
						0%	20%	50%
1	Small particles- 38-75 μ	.055	30	1.1	2.3	0.23	0.34	0.9
2	Big particles- 250-500 μ	0.08	150	1.13	2.7	0.04	0.2	0.35
3	100 ppm PEG	0.07	880	1.01	2.6	0.05	.021	0.28
4	200 ppm PEG	0.1	1150	1.055	2.35	0.05	.011	0.2
5	In coating	0.1	80	1.11	2.55	0.15	.02	0.5
6	500 ppm PbO	0.1	70	1.04	2.6	0.25	.04	-

Six samples were tested. The first sample consisted of small particles of zinc in the range of 38-75 microns. The rest of the samples contained large particles of zinc in the range of 250-500 microns. The second sample had no additives. The third and fourth contained 100 and 200 ppm PEG-600 in the electrolyte. The fifth sample had an indium-coated lining adjacent the zinc. The sixth sample contained 500 ppm PbO. Table 1 shows the results corrosion tests in which the cells were discharged at 0.47 A. The table headings are defined as follows: IR is the resistance of the test cell. Rp is the passivation resistance. V_{plat} is the plateau exhibited by the voltage vs. time discharge curve. Cap. is the total energy delivered before the voltage dropped below 0.9 volts. Corrosion rates were measured at various points through the discharge history of the test cells, namely, at 0% discharge, 20% discharge, and 50% discharge.

From Table 2 it can be seen that the corrosion rate of small particles is much greater than that of the larger particles. Addition of PEG reduced corrosion but reduced the plateau voltage and increased the passivation resistance. From these data, it is concluded that removing the smaller fraction of zinc from a batch of zinc particles reduces the corrosion rate. It has been found by further experiments that if the particles below 75 microns are removed

from a zinc batch, the corrosion rate is lowered to the point comparable to the above large particle samples. Preferably, the particles below 100 microns in size are removed.

Fig. 2 shows the effects of mechanical shocks on the discharge voltage of five (5) zinc-air battery cells, A, B, C, D, and E, having different proportions of PEG and having different porosities (the greater the concentration of PEG corresponds to lesser porosity). At times I, II, and III, the battery cells were dropped onto a rigid surface at increasing heights. As shown in the chart, PEG affects the cell's reaction to shock. At concentrations of 10 ppm, the battery cell experienced a drop of .135 volts or approximately 10% when dropped from a height of 10 cm. This drop was less than .02 volts, or 2%, when the PEG concentration was increased to 50 ppm. Increasing the concentration further results in a minor improvement in shock resistance with a significant drop in discharge voltage. Although the discharge voltage of the 10 ppm. cell benefited from the lower concentration levels, this benefit was more than offset by the shock effects when dropped more than 10 cm.

To increase the performance of the cell, especially when exposed to low temperatures, a low viscosity diluent can be added to the zinc electrolyte mixture. Examples of suitable diluents are isopropanol, isobutanol, and secbutanol, and long chain and branched alcohols. Concentrations of 5% by weight of a low viscosity diluent have been found to increase the discharge voltage by 60mV.

To increase the energy capacity of the cell, alumina (Al_2O_3) can be added to the zinc mixture. Concentrations of alumina of 1% by weight have been found to increase capacity by about 10%. However, the addition of alumina tends to decrease the discharge voltage of the cell. This voltage decrease can be offset through the addition of a diluent, as described above.

Referring to Figs. 3 and 4, the two graphs show the effects that alumina and isopropanol have on a battery cell when the battery cell is exposed to low temperature environments.

Figure 3 shows the discharge voltage of a battery cell with the additives at 25°C, and Figure 4 shows an identically-configured cell at 0°C. In the lower temperature environment (Fig. 4), both the discharge voltage and the energy capacity of a cell with the additives exceeded those of the cell without the additives. In the higher temperature environment (Fig. 3) the additives neither helped nor hurt the performance of the battery cell.

Corrosion resistance of the zinc anode is also accomplished through a coating on the metal casing. The zinc anode can react galvanically with the metal of the casing, resulting in corrosion and the generation of hydrogen (gassing). Gassing increases the internal pressure of the battery cell, which also increases the likelihood that the battery cell will leak. The

generation of hydrogen can cause a cell to fail within hours of assembly.

The following zinc/electrolyte/corrosion-inhibitor combination was formed as an example that displays the above properties.

1. 560 grams of zinc powder (thermal zinc) from Mitsui Mining & Smelting Co. Ltd., ABI grade is mixed with 5 grams of Carbopol 941, a gelling agent, to form a uniform zinc/gelling agent mixture.
2. 27.4 grams of ZnO from Durham, Electrolux grade, is mixed with a liter of deionized water, 8.5 M in KOH, to form zincate solution. Electrolytic zinc is formed by electroplating the zinc from the zincate solution onto a metal sheet. The electrolytic zinc is added to 435 grams of a deionized water solution of 8.5 M KOH from Oxychem Co. at a proportion of 22 grams of electrolytic zinc for every liter of deionized water to form a zinc/water solution.
3. The zinc water solution is mixed with the zinc/gelling agent mixture to form a blend containing 56.0:0.5:43.5 by weight of zinc powder:Carbopol:KOH. The blend is stored for 24 hours and separated into the desired dosage.

To limit gassing and corrosion, a layer of tin is coated onto the interior side of the casing, thereby separating the zinc anode from the metal casing. A complete electrical separation is not preferred since, in most zinc-air cells, the casing acts as an current collector of the cell, and the anode is electrically connected to this current collector through its contact with the casing.

The thickness and the manner of application play major roles in the effectiveness of the coating. Tests conducted on cells with a coating of indium of 11 microns and 33 microns revealed that the corrosion rate improved 320% - 900% from the thinner to the thicker coating. The average corrosion rate of a cell with a 11 microns thick coating of indium was 0.32% to 0.36% per week. This average decreased to 0.04% to 0.1% for a 33 microns thick coating.

Forming a uniform and complete coating of tin can be accomplished by soldering, electrolytic plating, and electroless plating. Tin can be soldered onto the surface of the casing by melting the tin and spreading it over one or both surfaces. Tin can also be added by an electrolytic process on either or both sides of the casing element. An electroless process can also be used. Applying tin through a well-known electroless process requires the presence of a copper support layer.

Referring now to Fig. 5 showing an anode casing element 100 formed of three layers of different materials, a layer of copper 105 forms the inner surface of the casing element 100, and a layer of nickel 110 forms the outer surface of the casing element 100. Between the two layers 105, 110 is a layer of stainless steel 115. The combination of the three layers 105, 110, and 115 provides the casing element 100 with material properties that are not found in a single material. The layer of nickel 110 provides the casing element 100 with improved electrical connectivity properties with the electronic device. The layer of nickel 110 also protects the layer of stainless steel 115 from the atmospheric conditions, which can cause the layer 115 to oxidize and corrode. The layer of stainless steel 115 provides strength to the structure of the casing element 100. The layer of copper 105 protects the layer of stainless steel 115 and the metal anode from reacting with each other and also provides a surface for the electroless plating of the protective layer of tin.

Copper is required for the electroless plating of tin. SnO or SnCl_2 reacts with the copper layer 105 in a bath containing thiourea. The layer of tin (not shown) formed on the copper layer 105 has been found to inhibit the corrosion of the metal anode.

The casing element 100 may also be formed of two layers instead of three, with the layer of nickel 110 eliminated. The nickel layer 110 does not assist with the inhibition of the reactivity between the zinc anode and the casing element 110, and is therefore, not absolutely essential to the benefit exhibited.

Further, a casing element may also have two layers of copper and one layer of stainless steel. For example, referring to Fig. 6 showing such an arrangement in an alternative casing element 120, a layer of copper 125 forms the inner surface of the casing element 120 and a layer of copper 125 also forms the outer surface of the casing element 120, with the copper layers 125 sandwiching a layer of stainless steel 130.

When this casing element 120 is immersed in a bath containing thiourea and SnO or SnCl_2 , layers of tin (not shown) are formed on both sides of the casing element 120. The layer of tin on the outer surface of the casing element 120 protects the casing element from corrosion in ambient air.

Another solution to the corrosion problem is to coat a substantial portion of the inner surface of the casing element with an insulator, such as an epoxy. Since the chemical reaction rate between the zinc anode and the casing element is directly related to the area of the exposed surface of the casing element to the zinc anode, a reduction of this exposed surface area reduces the rate of corrosion. However, some exposure should remain since the casing

element acts as a current collector of the cell, and electrical connectivity between the zinc anode and casing element should remain for the casing element to perform this function.

Examples of suitable insulting materials include tar and epoxy.

5 To further improve the performance the efficiency of the battery cell, a zinc/electrolyte mixture should contain a lesser concentration of zinc than the mixture employed in the prior art. Concentrations of 60% zinc by weight, instead of 70-80% zinc as used in the prior art, ensures that a greater portion of the zinc is utilized. Larger concentrations of zinc results in a drier mixture that is more susceptible to desiccation and the attendant decreased energy capacity. Metal-air battery cells are particularly susceptible to dry-out.

10 It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative embodiments, and that the present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather
15 than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed is:

1. A metal-alkaline battery cell comprising:
a cathode including a catalyst and a conductive material;
5 a first terminal electrically connected to the cathode;
a mixture including an electrolyte and particle-size-selected metal;
a second terminal electrically connected to the mixture; and
a separator located between the cathode and the mixture, in physical contact with the
cathode and with the mixture, said separator being of such material as to permit ions to travel
10 between the cathode and the mixture and to block metal particles from contacting the cathode,
wherein substantially all particles contained in the particle-size-selected metal are
larger than a predetermined size.
2. The battery cell of claim 1, wherein the wherein the particle-size-selected metal
15 includes particle-size-selected zinc.
3. The battery cell of claim 2, wherein the particle-size-selected zinc accounts for about
60% of the mixture by weight.
- 20 4. The battery cell of claim 2, wherein the mixture includes electrolytic zinc.
5. The battery cell of claim 4, wherein a ratio of electrolytic zinc to particle-size-selected
zinc in the mixture is between about 1:9 and about 1:1.
- 25 6. The battery cell of claim 4, wherein the electrolytic zinc and the particle-size-selected
zinc, taken together, account for about 60% of the mixture by weight.
7. The battery cell of claim 1, wherein the conductive material includes carbon.
- 30 8. The battery cell of claim 1, wherein the wherein the separator includes Teflon.
9. The battery cell of claim 1, wherein the mixture includes a gelling agent.

10. The battery cell of claim 1, wherein the particle-size-selected metal contains a substantial amount of particles with sizes that are close to the predetermined size.
11. The battery cell of claim 10, wherein the predetermined size is about 75 microns.
12. The battery cell of claim 11, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.
13. The battery cell of claim 10, wherein the predetermined size is about 100 microns.
14. The battery cell of claim 13, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.
15. The battery cell of claim 1, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected metal.
16. A metal-air battery cell comprising:
an air electrode;
a first terminal electrically connected to the air electrode;
a mixture including an electrolyte and particle-size-selected metal;
a second terminal electrically connected to the mixture; and
a separator located between the air electrode and the mixture, in physical contact with the air electrode and with the mixture, said separator being of such material as to permit ions to travel between the air electrode and the mixture and to block metal particles from contacting the air electrode,
wherein substantially all particles contained in the particle-size-selected metal are larger than a predetermined size.
17. The battery cell of claim 16, wherein the separator includes Teflon.
18. The battery cell of claim 16, wherein the particle-size-selected metal includes particle-size-selected zinc.

19. The battery cell of claim 18, wherein the particle-size-selected zinc contains a substantial amount of particles with sizes that are close to the predetermined size.
20. The battery cell of claim 19, wherein the predetermined size is about 75 microns.
21. The battery cell of claim 20, wherein substantially all particles contained in the particle-size-selected zinc are smaller than about 500 microns.
22. The battery cell of claim 19, wherein the predetermined size is about 100 microns.
23. The battery cell of claim 22, wherein substantially all particles contained in the particle-size-selected zinc are smaller than about 500 microns.
24. The battery cell of claim 19, wherein the mixture includes a gelling agent.
25. The battery cell of claim 19, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected zinc.
26. The battery cell of claim 19, wherein the particle-size-selected zinc accounts for about 60% of the mixture by weight.
27. The battery cell of claim 19, wherein the mixture includes electrolytic zinc.
28. The battery cell of claim 27, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture is between about 1:9 and about 1:1.
29. The battery cell of claim 27, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% of the mixture by weight.
30. A method of forming a corrosion resistant metal-air battery cell comprising the steps of:
forming a mixture by mixing ingredients including an electrolyte and particle-size-selected metal;

electrically connecting a first terminal to the mixture obtained in the forming step;
obtaining an air electrode with a second terminal connected thereto; and
positioning a separator between the air electrode and the mixture, in physical contact
with the air electrode and with the mixture, wherein the separator permits ions to travel
5 between the air electrode and the mixture and blocks metal particles from contacting the air
electrode,
wherein substantially all particles contained in the particle-size-selected zinc are larger
than a predetermined size.

10 31. The method of claim 30, wherein the particle-size-selected metal contains a substantial
amount of particles with sizes that are close to the predetermined size.

32. The method of claim 31, wherein the predetermined size is about 75 microns.

15 33. The method of claim 32, wherein the particle-size-selected metal includes particle-
size-selected zinc.

34. The method of claim 32, wherein substantially all particles contained in the particle-
size-selected metal are smaller than about 500 microns.

20

35. The method of claim 31, wherein the predetermined size is about 100 microns.

36. The method of claim 35, wherein the particle-size-selected metal includes particle-
size-selected zinc.

25

37. The method of claim 35, wherein substantially all particles contained in the particle-
size-selected metal are smaller than about 500 microns.

38. The method of claim 31, wherein the particle-size-selected metal is obtained by
30 removing substantially all metal particles that are smaller than the predetermined size from a
batch of metal particles.

39. The method of claim 38, wherein a sieve is used to remove substantially all of the

metal particles that are smaller than the predetermined size.

40. The method of claim 31, wherein the mixture formed in the forming step includes a gelling agent.

5

41. The method of claim 31, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected metal.

42. The method of claim 31, wherein the particle-size-selected metal includes particle-size-selected zinc, and the particle-size-selected zinc accounts for about 60% by weight of the mixture formed in the forming step.

10

43. The method of claim 31, wherein the particle-size-selected metal includes particle-size-selected zinc, and the mixture formed in the forming step includes electrolytic zinc.

15

44. The method of claim 43, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture formed in the forming step is between about 1:9 and about 1:1.

45. The method of claim 43, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% by weight of the mixture formed in the forming step.

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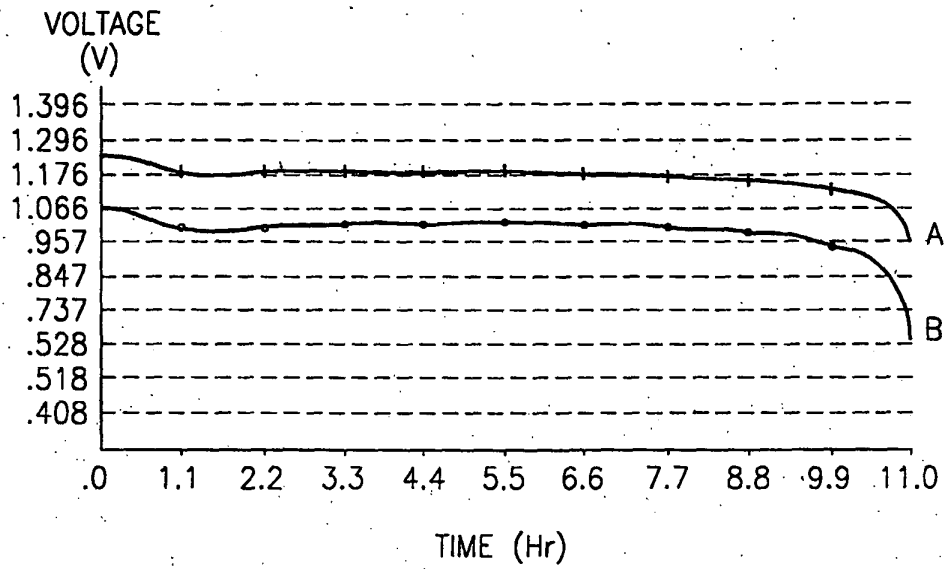


FIG. 1

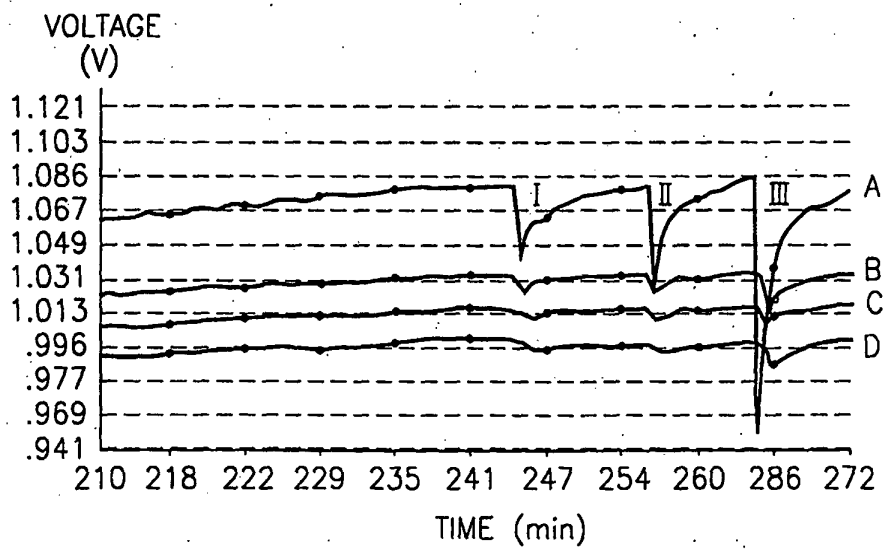


FIG. 2

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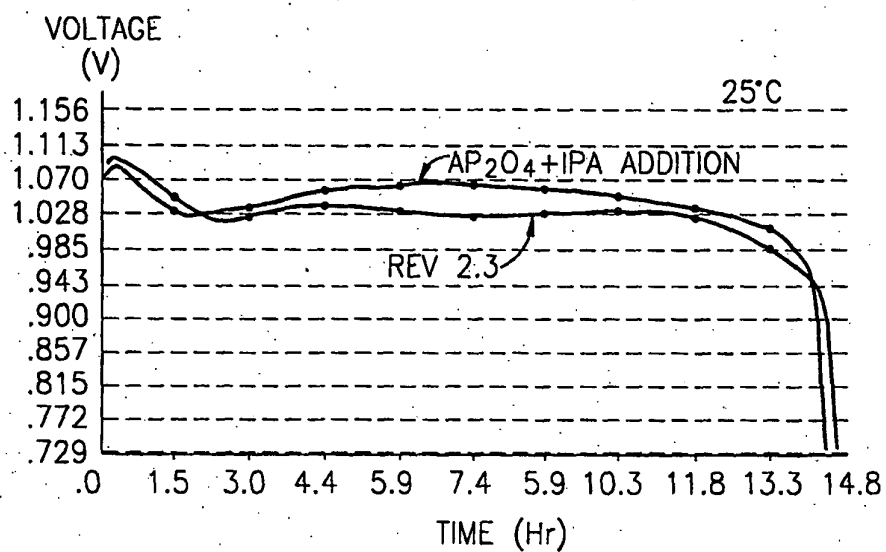


FIG.3

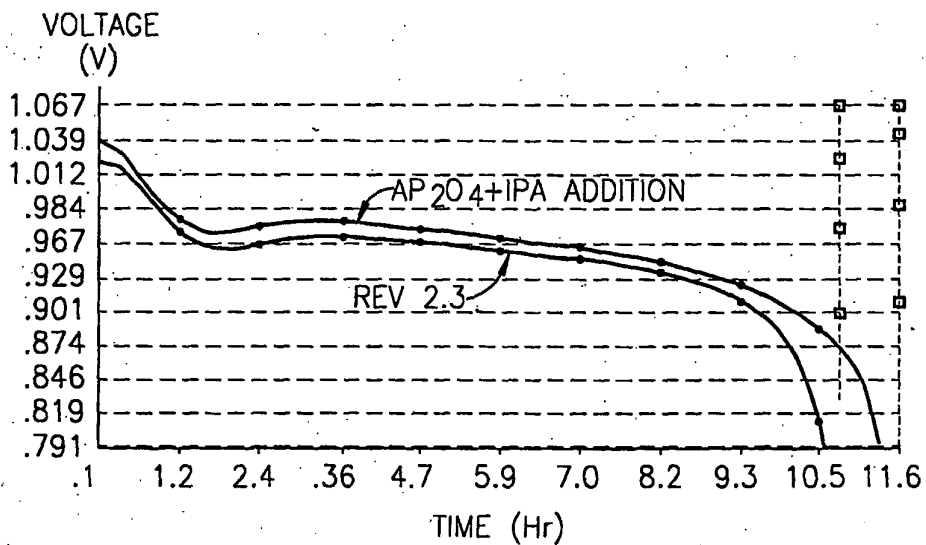


FIG.4

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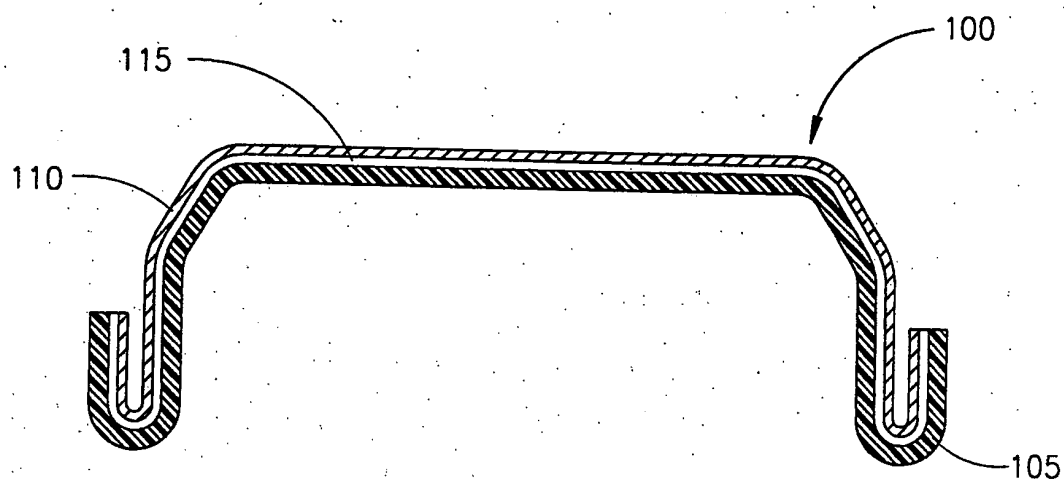


FIG. 5

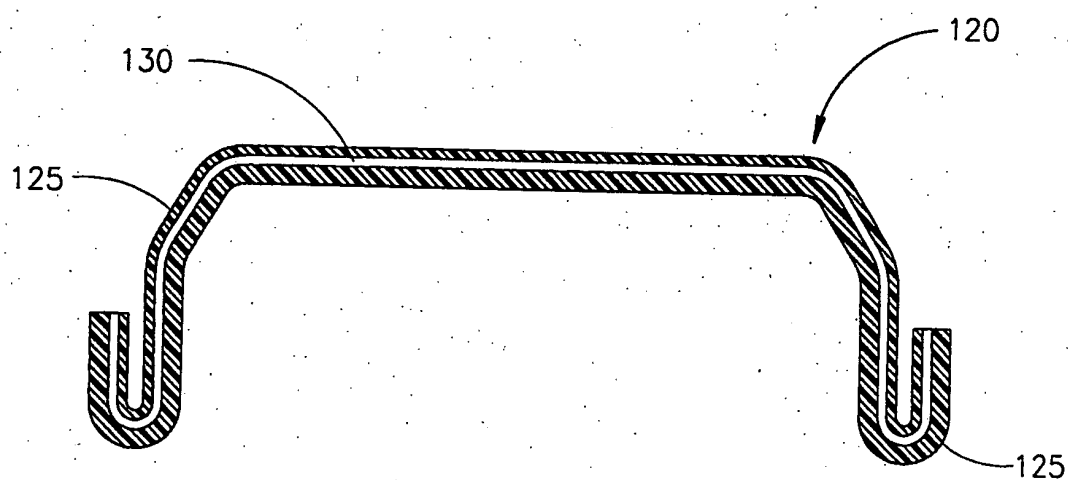


FIG. 6

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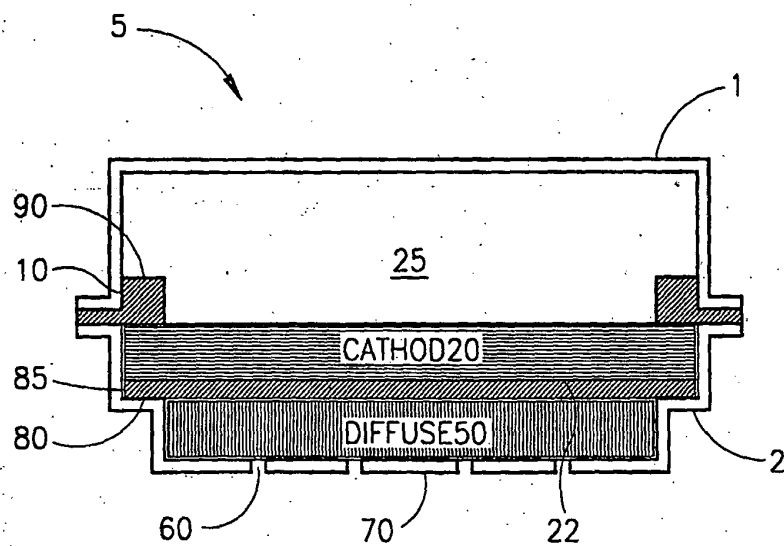


FIG.7

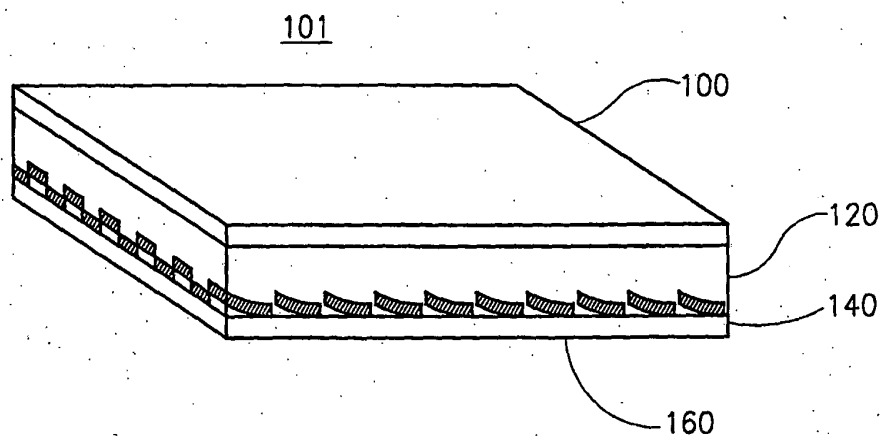


FIG.8

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IL 99/00681

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M12/06 H01M4/62 H01M8/22 H01M4/90

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 30 25 476 A (GOULD INC., ROLLING MEADOWS, US) 12 February 1981 (1981-02-12)	1,2,7,9, 10,16, 18,19
A	page 12, line 17 -page 17, line 3 figure 1	24
Y	PATENT ABSTRACTS OF JAPAN vol. 010, no. 087 (E-393), 5 April 1986 (1986-04-05) & JP 60 230359 A (PENTEL KK), 15 November 1985 (1985-11-15) abstract	1,2,7,9, 10,16, 18,19
A		11-14, 20-24, 30-37, 39,40
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

2 March 2000

Date of mailing of the international search report

13/03/2000

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Peis, S

INTERNATIONAL SEARCH REPORT

Int. nat. Application No

PCT/IL 99/00681

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